

Energetics of High Temperature Phase Transitions of Rare Earth Oxides

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The understanding of the phase stability and polymorphism of rare earth oxides is of great importance for applications at elevated temperatures, either by themselves, in solid solutions such as fluorite-based phases, or in multiphase composites. Below 2000 °C, rare earth oxides (RE_2O_3 , RE = La–Lu, as well as Y) show a variety of phases and phase transitions depending on the radius of the rare earth ion. Sm_2O_3 , Eu_2O_3 , and Gd_2O_3 are cubic C phase (IA-3, vacancy ordered defect fluorite) at ambient conditions and show a cubic to monoclinic B (C2/m) phase transition between 1100 and 1300 °C. The C to B transformation is of interest because it occurs with an increase in coordination number and increase in density, which is relatively unusual. These high temperature phase transitions are poorly characterized, in terms of reversibility, definitive analysis of phases formed, and thermodynamics.

The enthalpy of the C to B transition has been determined for Sm_2O_3 , Eu_2O_3 , and Gd_2O_3 , using a Netzsch DSC 404 differential scanning calorimeter and a Setaram HT96 scanning modified Calvet-type calorimeter operating to 1500 °C. All phase transitions are endothermic, which means the high temperature monoclinic B phase is stable above the transition but metastable at ambient conditions. Because the B phase can be quenched to room temperature, drop solution calorimetry was performed using custom-built Tian-Calvet calorimeters to determine the transition enthalpy for Sm_2O_3 , Eu_2O_3 , and Gd_2O_3 . These results are compared to the results from the DSC experiments, in order to crosscheck the methodology for the DSC calibration at 1200 to 1500 °C. This is a nontrivial issue because of the lack of suitable phase transition standards.